

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
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KINETICS OF BUTADIENE PRODUCTION - DEHYDROGENATION OF
MIXED n-BUTANE + BUTENES AT 1/6-ATMOSPHERE PRESSURE
EXPERIMENTAL RESULTS AND EMPIRICAL CORRELATIONS

By

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I. INTRODUCTION

In connection with Phillips continuing interest in butadiene production, data were desired for the conversion of n-butene to butadiene in a single stage and at less than atmospheric pressure. Earlier experimental data were limited to the conversion of pure n-butane to butenes + butadiene. For present considerations of this process, data were needed for the conversion of mixed n-butane + butenes (steady-state feed). In addition, data were desired for use in studies of n-butane and butenes dehydrogenation kinetics.

To accomplish these objectives, steady-state feed mixtures were dehydrogenated with 1/70-inch particles of chromia-alumina catalysts at 125 mm. mercury absolute pressure and over the temperature range of 1050 to 1250°F. Product distributions and reaction rates were calculated from the experimental results.

II. EXPERIMENTAL WORK

A. Apparatus and Equipment

The equipment used for the study of low pressure dehydrogenation reaction rates is schematically outlined in Figure 1. The total volume of the system was 8-9 cc and the reactor contained 2.2 cc. The schematic description of the furnace and reactor used for 1/70-inch catalyst particles is shown in Figure 2. Three-way solenoid valves were used to switch instantaneously between hydrocarbon and other gas feeds. Electrically heated furnaces were used to preheat the gases, to heat the catalyst and to produce a "heat seal" at the reactor outlet to minimize heat lost through the exit of the furnace. The preheat and catalyst furnaces were controlled with Wheelco Amplitrol temperature controllers which operated in conjunction with chromelalumel thermocouples located above the catalyst bed (for preheat furnace) and on the external wall of the catalyst zone (for the catalyst zone furnace). The heat-seal furnace was found to give better heat insulation if used in connection with Variac control only. Ceramic orifice gas flowmeters and Ideal needle valves were used to control the gas flows. Pressure control was manual and absolute pressure was measured at the reactor inlet and outlet with mercury manometers. The total effluent was collected and mixed with a Toepler pump. Samples of the total mixture were analyzed by gas chromatography.

B. Materials and Reagents

Catalyst was prepared by impregnating alumina granules with aqueous chromic acid solution, drying, calcining at 1000°F, and preparing a 40-50 mesh fraction by sieving. The catalyst was analyzed and found to contain 29.52 weight per cent Cr_2O_3 and .12 weight per cent Na_2O on dry basis. Surface area by B. E. T. method was found to be 70 square meters per gram.

Gases used for the tests were: (1) pure grade normal butane, pure grade butene-2, research grade ethylene and propylene from Phillips Chemical Company, (2) prepurified nitrogen and cylinder hydrogen from National Gas Company, (3) and building service air which contained 0.0006 grams of CO_2 per liter and approximately 0.0010 grams H_2O per liter.

C. Procedures

A standard procedure was adopted for testing the catalyst to insure reproducibility. When the catalyst was not in use it was usually heated with air going over the catalyst (and in some instances N_2) at a space rate of 1000. Approximately 2.0 cc of 1/70-inch particles were tested.

A test began by treating the catalyst with H_2 at atmospheric pressure for 10 minutes at a space rate equivalent to the hydrocarbon space rate to be used but not going below 1000 space rate. The system was evacuated, checked for leaks for a period of one minute. Immediately after the leak checking period the three-way solenoid on the reactor outlet was activated so there was no possibility of hydrocarbon in the by-pass pressuring back to the catalyst zone. Nitrogen was then turned on over the catalyst at a space rate equal to the hydrocarbon space rate and a moment later the hydrocarbon was turned on and allowed to exit through the by-pass. When the pressure in the reactor built up to the desired pressure of 125 mm Hg absolute (or to atmospheric as in the case of standard butane runs) the reactor outlet solenoid was deactivated so as to commute nitrogen and hydrocarbon below the reactor and control was maintained with one rate valve. The time for this operation was kept to a minimum and usually was accomplished in 2-3 minutes. After all flows and pressures appeared to be steady, a switch controlling the two three-way solenoids above the reactor was activated so that the gas flows were instantaneously reversed (i. e. hydrocarbon started going over the catalyst and nitrogen through the by-pass). An electric clock was connected with this switch so the time measurements were begun simultaneously with the introduction of hydrocarbon. At the same time the switch controlling the solenoids above the reactor was activated, a second switch was activated energizing the solenoid below the reactor. Thus the effluent was conducted into the sample collection system and the pressure in the reactor was manually controlled by a second rate valve. During the dehydrogenation period of three minutes, the by-pass and the reactor were maintained at the same operating pressure to minimize possible leaks through the reactor outlet solenoid. At the end of the dehydrogenation period, the three-way solenoid on the reactor outlet was deactivated and nitrogen was allowed to sweep out any residual hydrocarbon at the same space rate as that used for hydrocarbon. Flushing was conducted long enough to give time for all hydrocarbon to be swept out of the reactor and into the sample collection system. At space rates of 100, flushing was continued for about 7 minutes--the time being measured accurately. After all hydrocarbon was removed from the reactor the sample was "closed in" and the pressure was allowed to build up in N_2 to atmospheric. The sample was removed after the temperature, pressure and volumes were recorded. The sample was replaced with columns of $CaSO_4$ and Ascarite (asbestos impregnated with KOH) connected in series. Nitrogen was turned off and service air was started at 1000 space rate to remove hydrogen and polymer (as water and carbon dioxide) for about one hour.

Temperature measurements were made at six different locations. These are shown schematically in Figure 2. At two of the six locations double thermocouples were used--one for controlling and the other for recording temperatures. Thermocouples were located:

- (1) Externally between the reactor and the core midway down the preheater to indicate how efficiently the gases were heating to reaction temperatures.
- (2) Internally at the preheat outlet or about 1/4-inch above the catalyst bed and inside the thermocouple well. Here also is a second thermocouple used to control the temperature of the preheat furnace.
- (3) Internally at 1/4-inch below the catalyst bed and inside of the thermocouple well.
- (4) Externally between the catalyst reactor and heating core 1/4-inch above the catalyst bed and on the same horizontal axis as (2) above. This thermocouple usually gave lower temperature readings than (2) above because at this point the junction of the narrow preheat furnace and the broader reactor furnace allowed some heat to be lost. Eventually this thermocouple showed signs of radical behavior by giving lower temperature readings. However, it was not replaced because of the danger of dislocating other thermocouples in the process.
- (5) Externally between the catalyst reactor zone and the heating core and midway between the upper and lower catalyst zone. Two thermocouples were located at this position; one for control of the catalyst zone furnace and the other for temperature recordings.
- (6) Externally between catalyst reactor wall and catalyst heating zone core about 3/4-inch below the catalyst zone and at the upper edge of the heat seal reactor. Temperatures were adjusted so as to simulate adiabatic conditions. Before going on hydrocarbon, temperatures at positions 2, 3, 5 described above were maintained within $\pm 5^\circ F$ of the desired reaction temperature. Temperature readings were taken at one minute intervals and the temperature drop recorded. Tables showing temperature recordings therefore represent the average temperatures over the total dehydrogenation period. In actual practice perfect adiabatic conditions were not possible because some heat was supplied through the walls as the endothermic reaction took place.

Analysis of hydrocarbon samples were made by chromatographic procedures at room temperature employing a molecular sieve column for hydrogen, nitrogen, oxygen, methane and carbon monoxide, and a hexamethyl phosphoramine column for the remaining components. The maximum deviation for these analyses was around $\pm 5\%$ of each component which was present in the amount of 10% or less. For components present in larger amounts, the maximum deviation was $\pm 1-3\%$. Typical deviations are usually found to be around $\pm 1\%$ of each component.

TABLE I
RESULTS OF REPRODUCIBILITY STUDIES

| <u>Original Procedures</u> | | <u>Modified Procedures</u> |
|---|---------------------------------|-----------------------------------|
| <u>Differential Runs (b)</u> | <u>Integral Runs (c)</u> | <u>Integral Runs (c)</u> |
| <u>Conv. (a)</u> | <u>Conv. (a)</u> | <u>Conv. (a)</u> |
| 3.00 | 33.9 | 31.51 |
| 3.15 | 30.4 | 31.30 |
| 5.20 | 31.6 | 29.23 |
| 2.59 | 27.7 | 29.23 |
| 3.82 | 39.0 | 30.50 |
| 1.65 | 37.4 | |
| 2.50 | | |
| Mean 3.13 | 35.0 | 30.63 |
| Std.Dev. ± 1.13 ($\pm 36\%$ of mean) | ± 3.6 ($\pm 10\%$ of mean) | ± 1.06 ($\pm 3.5\%$ of mean) |

- (a) Conversion mols of butane destroyed per 100 mols of feed.
- (b) Conditions: 1100 F, 1/6 atmosphere absolute pressure, 3 minute dehydrogenation period; feed: the mixture obtained after 20 per cent of the butane is converted in an integral run using a steady state butane-butene mixture.
- (c) Conditions: 1100 F, 250 GHSV, feed: 60% butane 40% butenes (steady-state); 1/6 of an atmosphere pressure; 3 minute dehydrogenation period.

TABLE II
RANGES OF EXPERIMENTAL CONDITIONS

| | |
|-------------------------------|--|
| Pressure, mmHg | 760 ^(a) or 125 ^(b) |
| Temperature, °F | 1050, 1100, 1150, 1200, 1250 F |
| Space Velocity ^(c) | 100 - 7000 |

- (a) With n-butane feed only.
- (b) With mixed n-butane + butene feed only.
- (c) Volumes of feed (S.T.P.)/volume catalyst/hour

In practice dual analyses were run on each sample and if the deviations were normal they were averaged and these were used for computations.

Catalyst deposits were removed after each run by oxidation with air and measured by absorbing the water formed in a column of CaSO_4 and absorbing the CO_2 formed on Ascarite.

Conversion, yield, selectivity and reaction rate data were calculated with the IBM 7090 computer.

Precision studies were made to determine the reproducibility of results with the equipment and techniques that were employed. Table I presents precision data for differential and integral studies by the original techniques along with data after the equipment and techniques were modified in an attempt to improve reproducibility.

The results of this study show that the precision of integral runs is three times better than that for differential run. This is due to the problem of measuring small changes in reaction products resulting from the low conversions required for differential status. After modifying the procedures and equipment the precision was increased three-fold to a significantly good figure (± 1.06 standard deviation or 3.5% of mean). Precision data were not obtained for the differential runs using the improved techniques, but it is believed that a similar three-fold improvement would be found.

D. Ranges of Experimental Conditions and Data

Table II presents the ranges of experimental conditions used in this study. All possible combinations of these variables were not used; only pure n-butane was used as feed at one atmosphere and it only at a temperature of 1100°F . Sufficient levels of space velocity were used at most temperature levels to establish a butane conversion/space velocity profile. The resulting experimental data and calculated results are quite extensive and are not reproduced here.

Since one objective of the mixed feed runs was to obtain data representative of operation of a plant operating on "steady-state" feed, the feed composition was changed with the temperature level. Feed composition varied from approximately 62 mole % n-butane, 38 mole % butene-2 at 1050°F to 73 mole % n-butane at 1250°F .

III. CORRELATION OF DATA

As a result of using "steady-state" feeds, net butene conversion in all runs was zero plus or minus a few per cent. Therefore, correlation of butene conversion was not attempted.

The complicating feature of the correlation of the dehydrogenation data was the gradual decline in catalyst activity with time. Data taken over a short period of catalyst life, particularly early in the catalyst life, indicated that conversion could be well correlated with space velocity by an equation of the form:

$$x = \frac{f}{a + bf} \quad (1)$$

where

- x = fractional conversion, mols converted per mol of feed.
- f = reciprocal space velocity, ft^3 catalyst-hr per mol feed.
- a, b = empirical constants.

Reciprocal space velocity in terms of mols of feed rather than volume of feed was chosen as the independent variable to give the proper units for the rate of reaction calculated by taking the derivative of x with respect to f.

The normal butane dehydrogenation data obtained at atmospheric pressure and 1100°F . were used to determine the effect of catalyst age on conversion. A number of equation forms were tried; the only acceptable fit of the data was obtained with an equation of the form:

$$x = \frac{f}{a + c\theta d + bf} \quad (2)$$

where

- x = fractional conversion, mols converted/mol feed.
- f = reciprocal space velocity, ft^3 catalyst-Hr/mol feed.
- θ = age of catalyst, days.
- a, b, c, d = empirical constants.

A computer curve fit of the data gave the following values for the constants in equation (2):

- a = 0.13707
- b = 1.26470
- c = 4.18770×10^{-7}
- d = 2.84670

A comparison of the experimental and calculated conversions is shown in Figure 3.

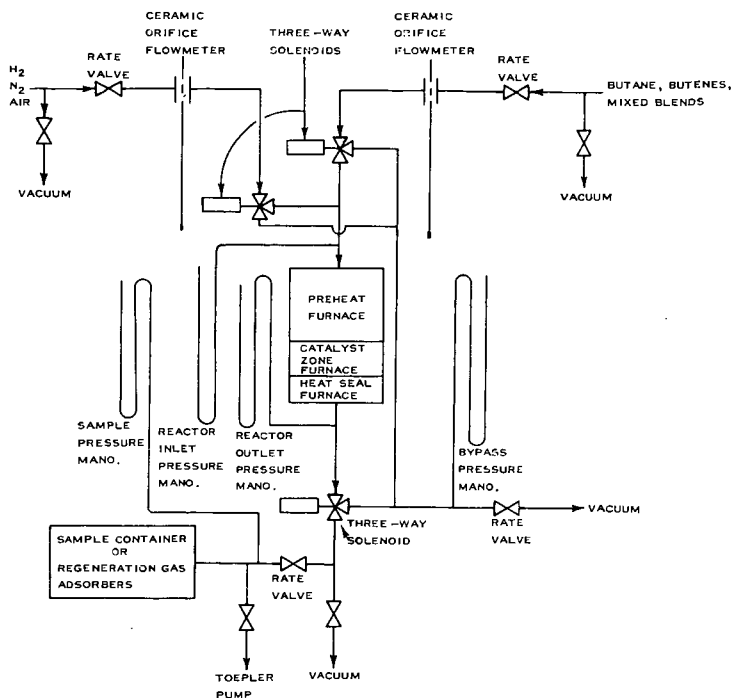


FIGURE 1
ASSEMBLY OF CATALYST TESTING EQUIPMENT

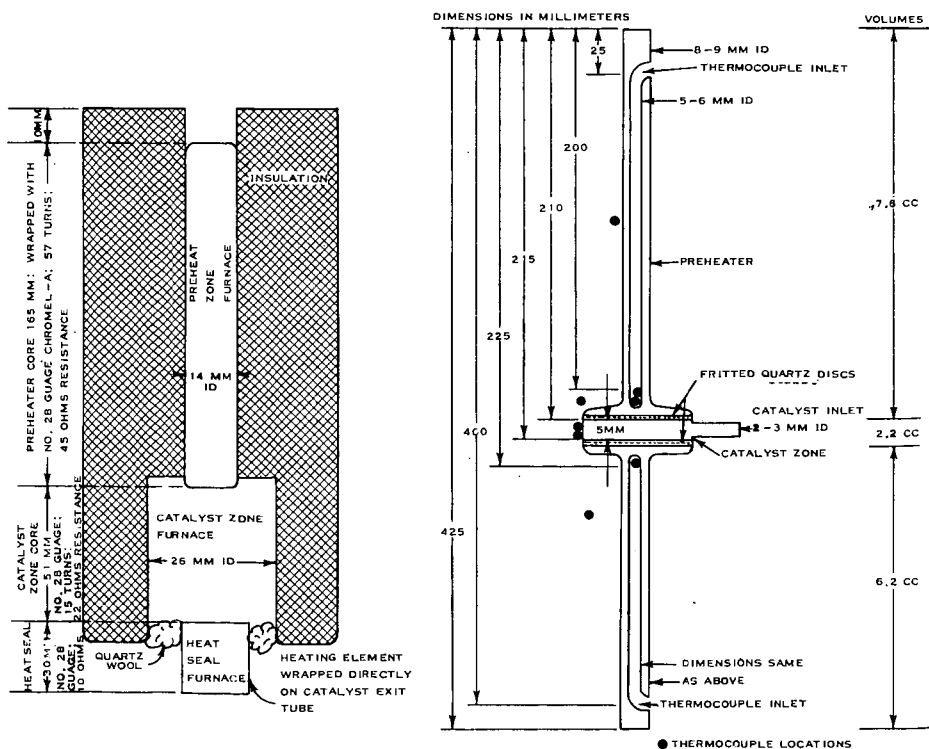


FIGURE 2
REACTOR AND FURNACE ASSEMBLY

There are a number of ways of expressing the activity of one catalyst relative to that of a second (or of the first at a different age). From the standpoint of reaction kinetics work, the preferred method (1) is to express the activity as the ratio of space velocities necessary to obtain the same conversion with the two catalysts. To obtain consistent correlations, it was desired to convert all the data available to their equivalent with a new (zero age) catalyst. For a zero age catalyst equation (2) reduces to:

$$x = \frac{f_0}{a + bf_0} \quad (2a)$$

where f_0 = reciprocal space velocity with zero age catalyst.

To find an expression for the equivalent space velocity with a zero age catalyst, equations (2) and (2a) are equated:

$$\frac{f_0}{a + bf_0} = \frac{f}{a + c\theta^d + bf} \quad (2b)$$

Solving this expression for f_0 in terms of f and θ gives:

$$f_0 = \left(\frac{a}{a + c\theta^d} \right) f \quad (3)$$

The quantity $\left(\frac{a}{a + c\theta^d} \right)$ is, in effect, the catalyst activity factor. Equation (3) was used to correct all the experimental space velocities for the mixed butane-butene feed data to their equivalents at zero catalyst age. In so doing it was tacitly assumed that the constants a , c , and d were not functions of temperature and pressure, or, if they were, that the effect of temperature and pressure were cancelled out by the form of the activity factor relation. It should be emphasized that this relation for activity is strictly empirical and must not be used with any other set of data or calculations without experimental confirmation.

The mixed butane-butene feed data were correlated as follows:

1. The experimental butane conversions, x_1 , where correlated as a function of the equivalent reciprocal space velocities, f_0 , calculated as outlined above in the form:

$$x_1 = \frac{f_0}{a + bf_0} \quad (4)$$

A separate correlation was obtained at each temperature level except 1200°F. At 1200°F. only three data points were available, all at essentially the same space velocity, so that a valid correlation could not be obtained.

2. The logarithms of the values of a and b obtained at each temperature level were plotted against reciprocal absolute temperature, Figure 4. From inspection of these plots, it appeared that the 1100°F points were out of line. These points were ignored and the remaining three points on each plot, representing data at 1050, 1150, and 1250°F., were fit to an equation of the form:

$$\ln a \text{ (or } \ln b) = \alpha + \beta \left(\frac{1}{T} \times 10^5 \right) \quad (5)$$

Evaluation of the constants gave the following results:

$$\ln a = -15.97115 + 0.25232 \left(\frac{1}{T} \times 10^5 \right) \quad (6)$$

$$\ln b = -1.82226 + 0.04281 \left(\frac{1}{T} \times 10^5 \right) \quad (7)$$

where $T = ^\circ R, ^\circ F + 460$.

As a test to justify ignoring the 1100°F. points, equation (6) was used to calculate a at 1200°F. This value of a and equation (4) were then used to calculate a value of b from each of the three data points available at 1200°F. The three values of b were then averaged. This average value of b was identical with the value calculated by equation (7) for 1200°F. It was concluded that ignoring the 1100°F. points was justified since the 1200°F. data had not been used to develop equations (6) and (7).

To check the overall correlation, equations (6) and (7) were used in conjunction with equation (4) to calculate a butane conversion value for each experimental point. Figure 5 shows a plot of observed versus calculated butane conversion and Figure 6 shows the experimental data plotted as conversion versus equivalent reciprocal space velocity; constant temperatures lines are shown calculated from equations (4), (6), and (7). The standard error of estimate for predicting butane conversion is 0.02429, very close to the standard deviation of replicate experimental determinations.

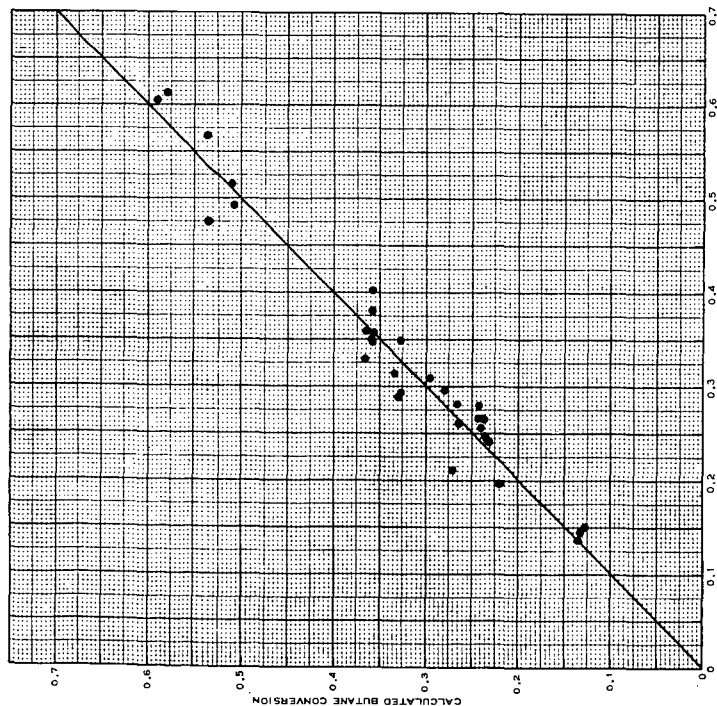


FIGURE 3
CALCULATED VS OBSERVED BUTANE CONVERSION
s - BUTANE FEED, 1100 F., 1 ATM

$X = 0.13707 + 4.10770 \times 10^{-7} \cdot \frac{1}{t}$
 $X = \text{FRACTIONAL BUTANE CONVERSION, MOLES/MOL FEED}$
 $t = \text{RECIPROCAL SPACE VELOCITY, CU. FT. CATALYST - HR/MOL FEED}$
 $\bullet = \text{CATALYST AGE, DAYS}$

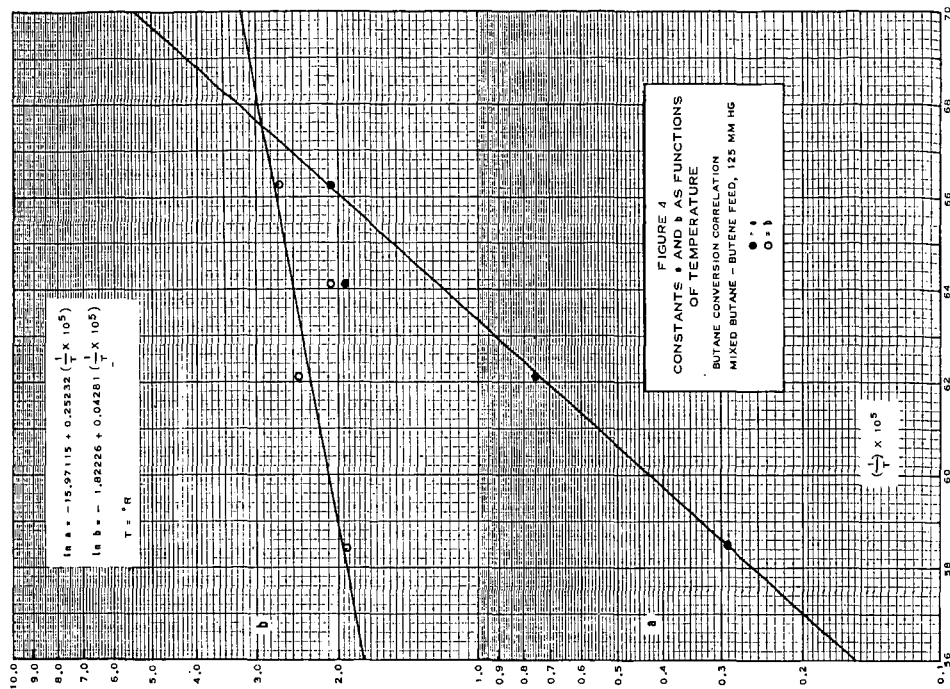


FIGURE 4
CONSTANTS a AND b AS FUNCTIONS
OF TEMPERATURE
BUTANE CONVERSION CORRELATION
MIXED BUTANE - BUTENE FEED, 125 MM HG

$\ln a = -15.97115 + 0.23232 \left(\frac{1}{T} \times 10^5 \right)$
 $\ln b = -1.82226 + 0.04281 \left(\frac{1}{T} \times 10^5 \right)$
 $T = ^\circ R$

A similar correlation procedure was used to correlate the data on butadiene appearance. At each temperature level (except 1200°F.), the data were fit to:

$$x_2 = \frac{f_o}{a + bf_o} \quad (4a)$$

where x_2 = butadiene appearance, mols per mol of feed. To be consistent with the result for butane disappearance, the 1100°F. data were ignored, and the a and b values for 1050, 1150, 1250°F. fit as functions of temperature. The results were:

$$\ln a = -13.03794 + 0.19267 \left(\frac{1}{T} \times 10^5 \right) \quad (6a)$$

$$\ln b = -4.48793 + 0.09814 \left(\frac{1}{T} \times 10^5 \right) \quad (7a)$$

Figure 7 shows plots of equations (6a) and (7a) with the data points. A check calculation at 1200°F. confirmed the validity of ignoring the 1100°F. data. Figure 8 shows a plot of observed versus calculated butadiene appearance and Figure 9 shows the experimental data plotted as appearance versus equivalent reciprocal space velocity, with constant temperature lines calculated from equations (4a), (6a) and (7a). The standard error of predicting butadiene appearance is 0.01414.

By differentiating the equation expressing conversion as a function of reciprocal space velocity with respect to reciprocal space velocity, an expression is obtained for the rate. Thus, for butane disappearance the rate is:

$$r_1 = \frac{a}{(a + bf_o)^2} \quad (8)$$

and for butadiene appearance the rate is:

$$r_2 = \frac{a}{(a + bf_o)^2} \quad (8a)$$

where r_1 = mols butane converted/ft³ catalyst-hr.

r_2 = mols butadiene produced/ft³ catalyst-hr.

f_o = equivalent reciprocal space velocity for zero age catalyst, ft³ catalyst-hr/mol feed.

a and b = constants calculated from equations (6) and (7) for butane or (6a) and (7a) for butadiene.

IV. DISCUSSION

In preparation for this study, the two well known methods of obtaining reaction rate data were compared, viz., differential experiments (using various feed mixtures which represent the total product at various locations in the reactor, and a relatively short residence time to give a small conversion), and integral experiments (using a feed mixture which represents the steady-state feed to the reactor, and various residence times to give various conversion levels). Based on this comparison, the integral experimental method was chosen because it gave more precise results than were given by differential experiments. This resulted from the relatively large changes in feed composition which occurred in the integral experiments compared to the relatively small changes in differential experiments.

In this work to obtain data for use in studies of n-butane and butenes dehydrogenation kinetics, temperatures above those normally used with chromia-alumina catalysts were employed. This caused a reduction in catalyst activity and required the use of a catalyst activity index. The value of this index was established at frequent intervals by testing the catalyst for the dehydrogenation of steady-state feed at 1100°F. This index has been used in correlations of these data; however, it may not be entirely satisfactory according to recent tests. These tests with pure n-butane and pure butenes showed that aging or heat-treating the chromia-alumina catalyst reduced its activity for n-butane dehydrogenation but did not affect its activity for butenes dehydrogenation. Data for the 1100°F. profile are questionable because they were obtained before the experimental procedure and equipment were entirely satisfactory. Some of the reasons for the unreliability of the data were: (1) flow rates in the catalyst zone varied widely during each test due to the relatively large volume of the gas handling system, and (2) the product sampling procedure did not insure collection of the total product from a test. These problems affected only the 1100°F. data for the steady-state feed.

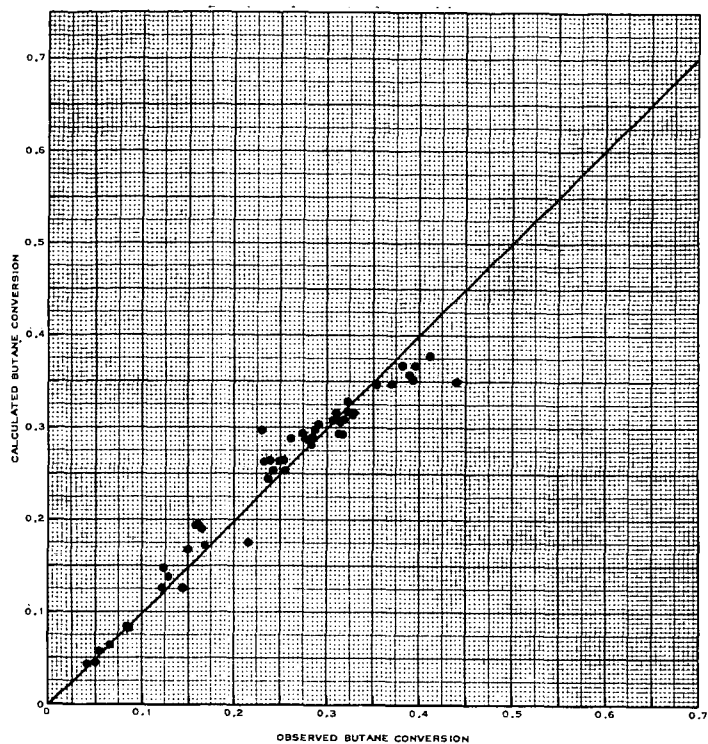


FIGURE 5
CALCULATED VS OBSERVED BUTANE CONVERSION

MIXED BUTANE-BUTENE FEED, 125 MM HG
1050 F, 1100 F, 1150 F, 1200 F AND 1250 F

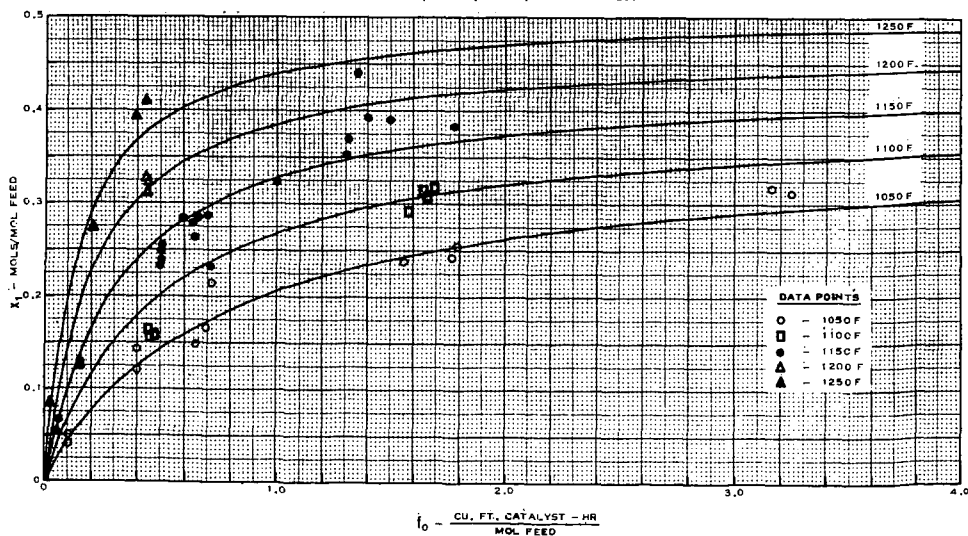


FIGURE 6
BUTANE CONVERSION
VS
EQUIVALENT RECIPROCAL SPACE VELOCITY

The correlations developed appear to fit the data within the experimental accuracy. Figure 3 shows a slight trend toward a breakdown of the butane conversion correlation at high conversion levels.

It must be emphasized that the correlations are empirical and care must be exercised in their use. Within the range of operating variables covered the correlations are adequate for process design work. Their most effective use, however, may be to use them to smooth the experimental data prior to evaluation of reaction mechanism type equations. The use of the correlations in this manner will give an internally consistent set of values for rates to evaluate the constants in reaction mechanism equations.

V. CONCLUSIONS

From the results of this study it is concluded that the conversion of n-butane and the appearance of butadiene in the dehydrogenation of n-butane can be satisfactorily correlated as functions of reciprocal space velocity using a two constant hyperbolic equation. The two constants of this equation can in turn be satisfactorily correlated as functions of temperature by an Arrhenius type equation.

Within the range of the variables studied the resulting equations are suitable for process design work. The equations should also be useful in smoothing the experimental data to obtain rates for a mechanistic type study of the reaction kinetics.

VI. LITERATURE CITED

- (1) Hougen, O. A., and Watson, K. M., "Chemical Process Principles, Part Three, Kinetics and Catalysis", p. 936. John Wiley and Sons, Inc., New York, 1949.

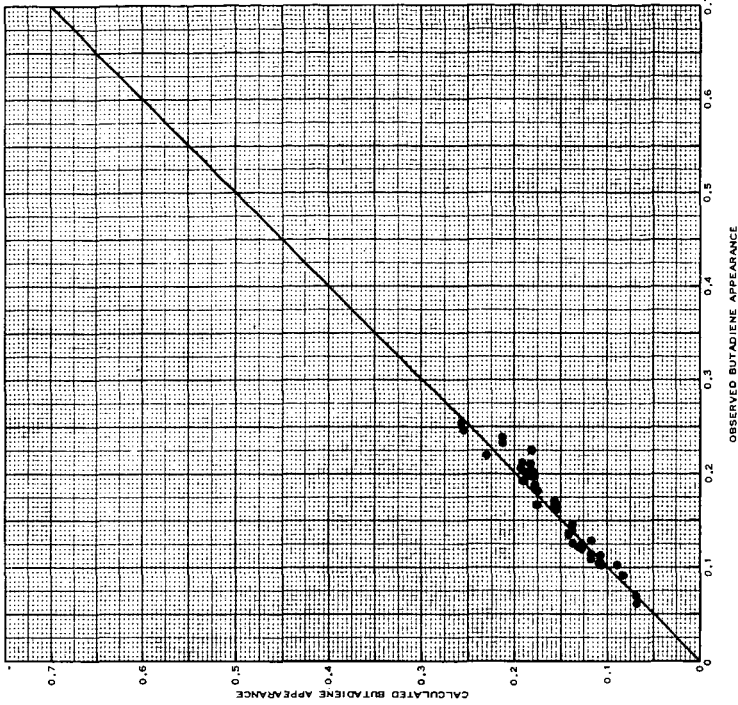


FIGURE 8
CALCULATED VS OBSERVED BUTADIENE
APPEARANCE (MOLS/MOL FEED)
MIXED BUTANE-BUTENE FEED, 125 MM HG
1050 F, 1100 F, 1150 F, 1200 F AND 1230 F

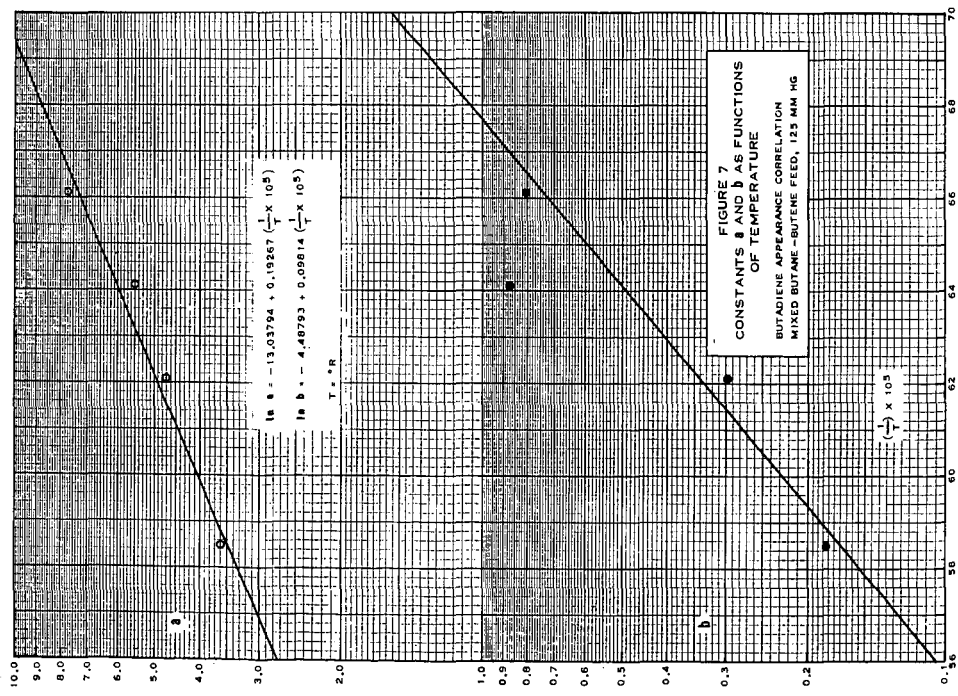


FIGURE 7
CONSTANTS a AND b AS FUNCTIONS
OF TEMPERATURE
BUTADIENE APPEARANCE CORRELATION
MIXED BUTANE-BUTENE FEED, 125 MM HG

